STUDIES ON FABRICATION, CHARACTERIZATION AND OPTICAL PROPERTIES OF DOPED CHITOSAN AND PULLULAN COMPOSITE FILMS

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The thesis entitled "**Studies on fabrication, characterization and optical properties of doped chitosan and pullulan composite films**" deals mainly with the fabrication, characterization, and applications of doped chitosan and pullulan films. The work is divided into six chapters.

CHAPTER 1: Review on recent development in optoelectronic applications of chitosan and pullulan biopolymers

CHAPTER 2: The studies on optical properties of hybrid chitosan films doped with new 1, 3, 4-oxadiazole derivatives

CHAPTER 3: The structural and photoluminescence studies of 2-[(4-tert-butylphenyl)-5–(4-biphenyl)]-1, 3, 4- oxadiazole (PBD) incorporated *γ* ray irradiated chitosan films

CHAPTER 4: The structural, UV and photoluminescence studies of 4,4'-bis(9*H*-carbazol-9-yl) biphenyl (CRB) incorporated *γ* ray irradiated chitosan films

CHAPTER 5: Design, fabrication and studies on optical properties of new hybrid chitosan films doped with 3-hydroxyflavone (3HF)

CHAPTER 6: Effect of nano ZnO Doping on Structural, Morphological and Luminescent Properties of Pullulan Films

CHAPTER 1

Review on recent development in optoelectronic applications of chitosan and pullulan biopolymers

1.1 Biopolymer composites in optoelectronic applications

Research in the field of optical properties of polymeric material mixing with two or more component has gained momentum in recent years [1][2][3]. The hybrid polymeric materials containing low molecular weight compounds which are dispersed in an insulating polymeric matrix have tremendous applications as high; performance photonic materials [4], nanogap films for nanogap sensors [5], luminescent solar concentrators [6], photochromic materials[7], photoluminescence yarns. Also dispersing low molecular weight organic compound into the polymeric matrix tends to form new hybrid material which differs in its properties compared to pure state that leads to new avenues for the application in the optoelectronic devices [8].

Biopolymers, based on biomaterials such as wool, leather, silk, and cellulose, have been utilised by mankind as food, clothing, and furniture from ancient times. However, such polymers can now be tailored to fulfil specific requirements. Biopolymers from natural and modern industrial economies play a major part in both ecosystems, as humankind lives in both natural and manufactured surroundings. Natural polymer-based products are becoming increasingly popular as a result of rising environmental concerns [9].

These biopolymers can also be divided into mainly three classes based on the monomer units, namely, polysaccharides, proteins and polynucleotides. Generally, polysaccharides are made up of sugar units which are covalently bonded each other through glycosidic linkage [10]. Proteins, on the other hand, are polymers made up of monomeric amino acid moieties. The amide linkages that join these amino acids to form a three-dimensional (3D) structure. The molecular interactions, including hydrogen bonding, salt and disulphide bridges, and hydrophobic and hydrophilic interactions tends to form a secondary structure of the protein ((e.g., α-helix, β-pleated sheets). One more class of biopolymer is polynucleotides such as DNA and RNA consisting of more than 13 or more monomer nucleotide monomer units. They serve a specific biological purpose in terms of storing, replicating, and analysing genetic data [11] (Fig.1)

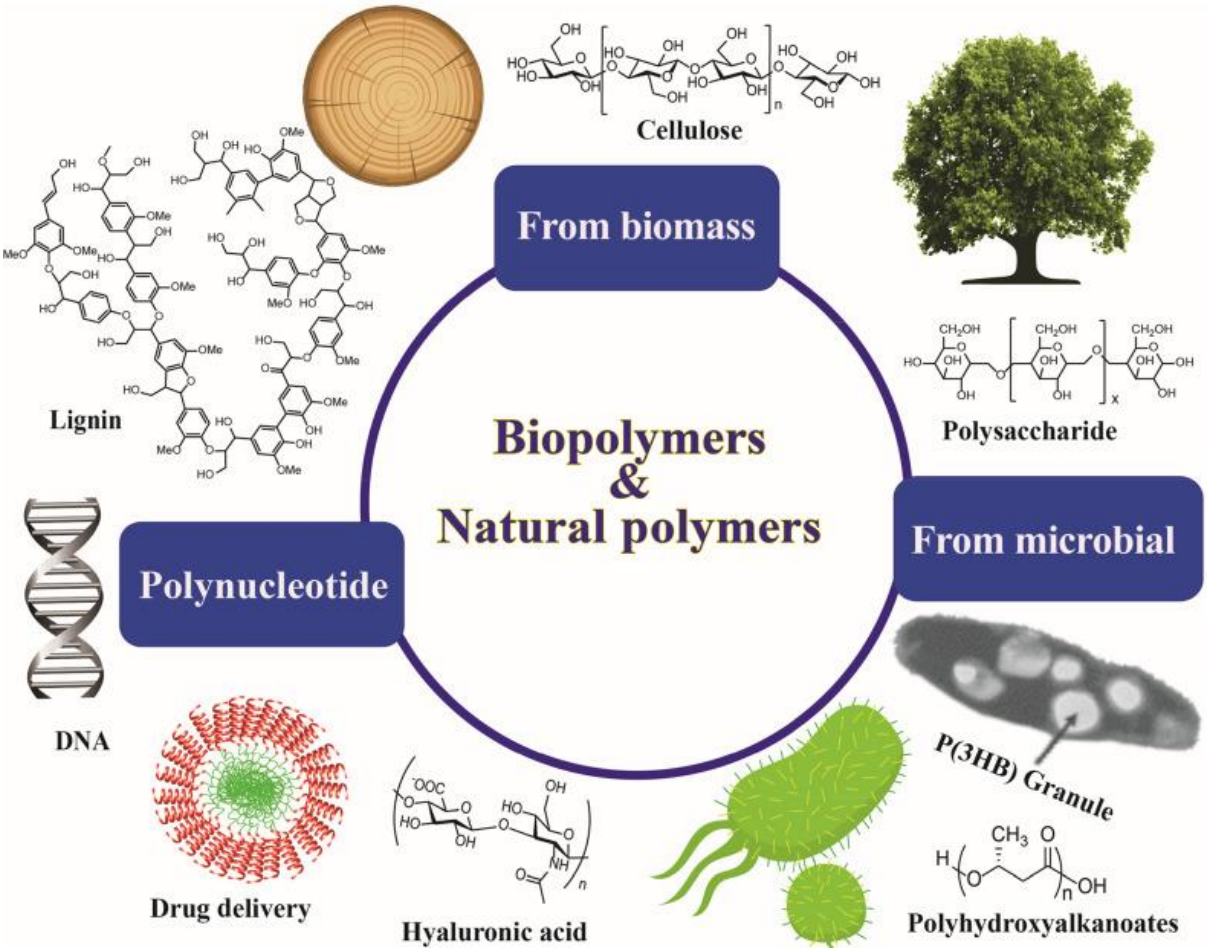


Fig.1. Classifications of polymer

In recent years, there has been a growing demand for a clean and pollution-free environment and an evident target to minimizing fossil fuel. Therefore, a lot of attention has been focused on research to replace petroleum-based commodity plastics by biodegradable materials arising from biological and renewable resources. Therefore, biocomposites are advantageous for a wide range of applications, such as medicine, pharmaceutics, cosmetics, food packaging, agriculture, forestry, electronics, transport, construction, and so forth (Fig.2).

Biopolymers possess natural electrical and optical properties which could be monitored [12][13]. Therefore, biopolymers could be potential alternative of the conventional manmade polymers. Biopolymers are special types of polymers that biodegrade with the action of microorganisms, heat, and moisture. Which could be isolated from bioresources, agri waste, fish waste. In recent times, a lot of investigations have been conducted on biomaterial-based nanocomposite resources as they are abundant, environment-friendly, and biodegradable. Such research fostered the application of bio composite materials attained from abundant plant resources as substrates for OLEDs (Organic Light Emitting Diode). This would serve the aspiration by fulfilling all the desired optical, thermal, and mechanical properties required

for the substrates and ultimately reducing the overall production cost. Also using biocomposite materials offer biodegradability and environmental-friendly aspects [14]. Thus, this work opens a new possibility of applications of bio resource–based biocomposites in optoelectronics industry.

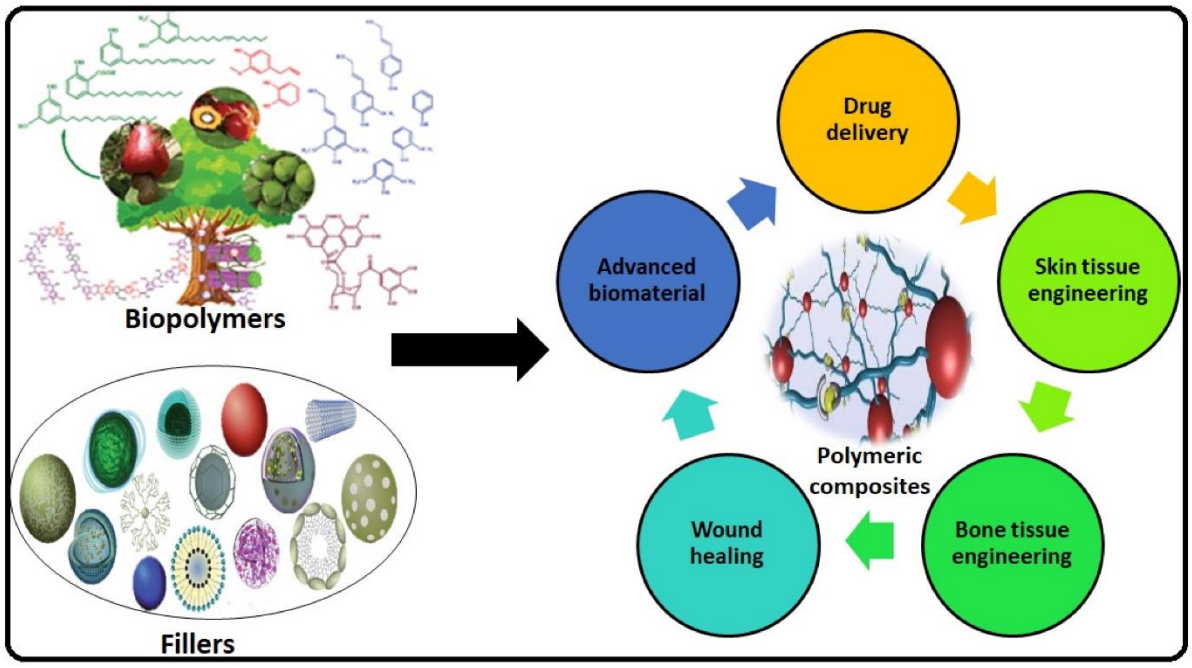


Fig.2. Applications of biopolymer

1.2 Chitosan

Chitosan is the *N*-deacetylated derivative of chitin [15]. Chitin and chitosan are of commercial interest due to their high percentage of nitrogen (6.89%) compared to synthetically substituted cellulose (1.25%). The application of biopolymers such as chitin and chitosan are one of the emerging adsorption methods for the removal of dyes and heavy metal ions, even at low concentrations. Chitosan is known as an ideal natural support for enzyme immobilization because of its special characteristics such as hydrophilicity, biocompatibility, biodegradability, non-toxicity, adsorption properties, etc. Chitosan can be used as an adsorbent to remove heavy metals and dyes due to the presence of amino and hydroxyl groups, which can serve as the active sites (Fig.3.) [[16][17][18]. Most of the naturally occurring polysaccharides, e.g., cellulose, dextran, pectin, alginic acid, agar, agarose and carragenans, are neutral or acidic in nature, whereas chitin and chitosan are examples of highly basic polysaccharides. Their unique properties include polyoxysalt formation, ability

to form films, chelate metal ions [19]. Chitosan, the deacetylated product of chitin, is soluble in dilute acids such as acetic acid, formic acid, etc. Recently, the gel forming ability of chitosan in *N*-methylmorpholine *N*-oxide and its application formulations has been reported [20]. Chitosan may be used to inhibit fibroplasia in wound healing and to promote tissue growth and differentiation in tissue culture. Chitosan is non-toxic and easily bioabsorbable with gel-forming ability at low pH. Also, chitosan matrix formulations appear to float and gradually swell in an acid medium. All these interesting properties of chitosan make this natural polymer an ideal candidate for controlled drug release formulations [21].
Chitosan, a nitrogenous polysaccharide with abundant of hydroxyl groups and amine groups, shows great hydrophilic properties and has strong affinity with lithium polysulfide to potentially minimize their loss into the electrolyte [22]. Due to its unique molecular structure, chitosan has an extremely high affinity for many classes of dyes, including disperse, direct, reactive, acid, vat, sulfur and naphthol dyes[23] . As for chitosan, it is one of the most plentiful natural biopolymers produced from chitin and is widely used in molecular separation, water treatment and other fields[24] . Moreover, it possesses good viscosity so it can be used as e polysulfide trapping agent in lithium-sulfur batteries [25].

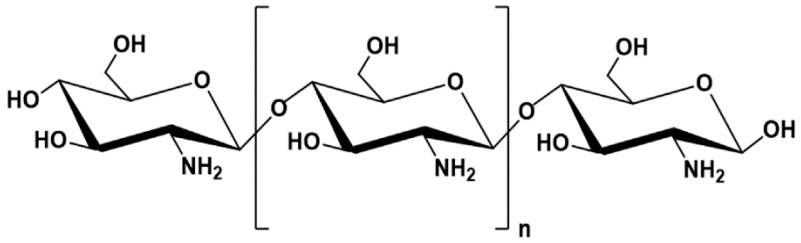


Fig.3. Structure of Chitosan

1.3 Pullulan

Pullulan is a well-known neutral polysaccharide with many applications in the food, cosmetic and pharmaceutical industries [26]. Pullulan due to its specificity for liver has been widely exploited for biomedical applications [27]. Among polysaccharides, pullulan is a promising material for biotechnological applications because it is a biocompatible and biodegradable polymer. Neutral and ionic pullulan derivatives have been also extensively developed for several applications including coating and packaging material, sizing agent for paper or starch substitute in low-calorie food formulations, and cosmetic emulsions [28][29]. Pullulan,

a microbial polysaccharide of α-1,6 linked maltotriose, has highly water solubility and flexibility of the chain in spite of the linear and regular backbone (Fig.5.) [30][31]. Therefore, the high solubility of pullulan might come from the high degree of the motional freedom around the linkage between glucose units. As the aqueous solution of pullulan is available in a wide range of concentration and stable in the wide temperature range, pullulan seems to be proper object in order to understand the hydration property better. The films and gels of pullulan possess porous 3-dimensional structure and high surface area that would benefit air permeation, moisture absorption, and action of active agents. Fibre mats made of pullulan are thus potentially useful in certain food applications, e. g. food packaging materials, and biomedical applications, e. g. wound dressing and drug delivery[32] .

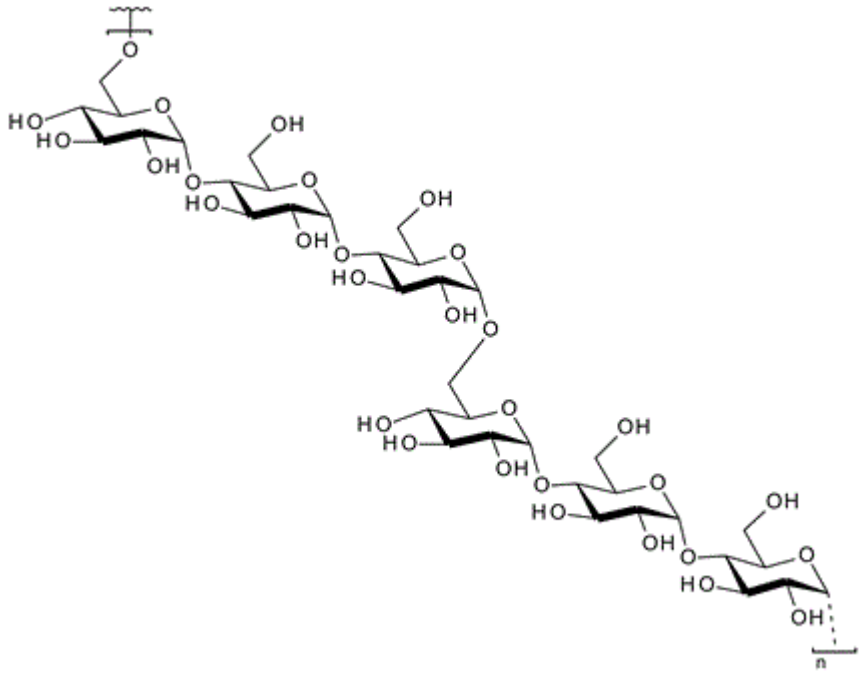


Fig.4. Structure of Pullulan

1.4 Dopant-matrix interaction for the enhancement of properties of polymer composites

The synthetic and natural polymer composites have been increasingly focused in terms of electrical and optical properties because of legibility to be utilized in batteries, fuel cells and capacitors [33]. The interest in dealing with the nature of the light interaction with such new materials increase, especially changing from solar cells to light-emitting devices. Moreover, due to those polymers that possess unique optical properties are taken into consideration to be utilized for optical devices, sensors and LEDs as well. To change the optical properties of certain polymers, it is viable to tune these properties using dopant materials.

There are many kinds of nanofillers (NFs), mixing of inorganic nanoparticles (NPs) that are incorporated into polymer matrices, resulting in nanocomposites (NCs) of polymer and inorganic materials combination. This is of technological importance owing to their prospective uses as magneto-optic and optoelectronic devices [34]. The most commonly used inorganic NFs are semiconductors, for instance, Ge, PbS, CdS and metal oxides (ZnO and TiO_2) as well as metals (Ag and Cu) and metal alloys (Co/Pt and Au/Pt). It is worth mentioning that this enhancement in optical properties of polymers opens the opportunity to be utilized in colour filters, polarizers, light-emitting diodes, optical communication devices, data storage devices and in the biomedical areas as well.

1.5 Organic dopant-matrix interaction

Polymeric materials having the optical properties, particularly, the ability to participate in energy or electron transfer processes are becoming increasingly important in the recent years. The good optical and mechanical properties of Schiff base polymers can be controlled optically [35][36]. In the beginning, inorganic material composites were mainly studied and these were found to be difficult to process and fabricate. On the other hand, these were too expensive. Because of these disadvantages of the inorganic materials, the efforts to find new hybrid materials for nonlinear optical [NLO] materials were focused on organic materials [37][38]. The organic polymeric materials posed more advantageous over inorganic polymeric materials for structure modification, good processibility into thin films, large susceptibility, high laser damage threshold, faster response time, etc. The cross-linked polymers exhibit even greater stability of optical activity than the host–guest system, but a significant optical loss occurred as a result of limited uniformity of the cross-linking reaction [39].

1.6 Research Gap

The hybrid materials offer better properties to design new devices. Oxadiazole derivatives and carbazole derivatives have proven as OLED materials and they were being used as electron and hole transport layers in OLED devices. In order to enhance the stability and usability of these compounds as well as other dopants, chitosan and pullulan-based hybrid materials could be taken up for the study. Hence following objectives were proposed.

1.7 STUDY OBJECTIVES

- To fabricate small molecules doped biopolymer films of chitosan and pullulan by solvent casting technique.
- To study the properties and stability of the films upon gamma irradiation.
- To characterize doped chitosan and pullulan films using morphology (SEM, PXRD), mechainical, thermal (TGA) and structural studies (FTIR)
- To study the optical properties namely UV-vis spectroscopy absorption and photoluminescence characteristics.

CHAPTER 2

The studies on optical properties of hybrid chitosan films doped with new 1, 3, 4-oxadiazole derivatives

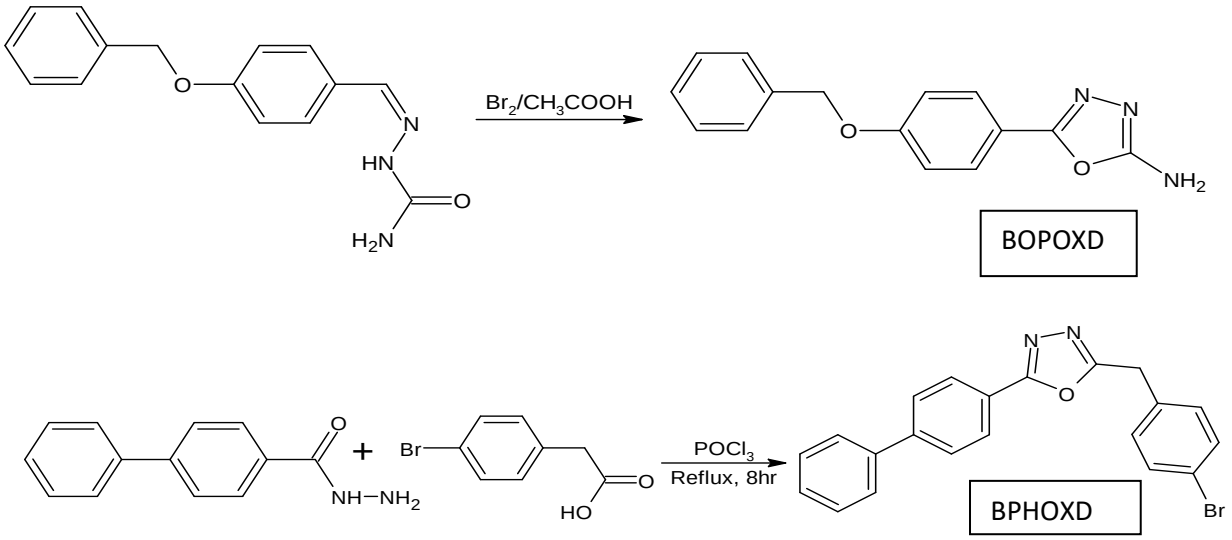
2.1. Introduction

In recent years, the technique of dispersing the chromophoric group like anthraldehyde[40], terepthaldehyde [41], 2-thiophenecarboxaldehyde [42] into the chitosan matrix to form conjugates by chemical cross-linking exhibited superior optoelectronic properties compared to pristine form. But the dispersing of azomethine based compounds in poly(methyl methacrylate), polysulfone and chitosan matrix resulted in dye dispersed nanocrystalline composite films [8]. The presence of azomethine was found be to the reason for enhanced photoluminescence.

Hence dispersing luminescent dyes in a polymer matrix provide an advantage to fabricate usable films which can be integrated into the devices. The 1, 3, 4-oxadiazole derivatives which were used as electron-transport materials in organic light emitting diodes [OLED] [43][44] could be doped into the polymer matrix as host molecules. The derivatives of 1, 3, 4-

oxadiazole have also been reported to have good quantum efficiency in red, green, blue OLEDs. The efficiency and brightness of the LEDs could be increased by derivatizing 1, 3, 4-oxadiazole moiety [45]. The 1,3,4- oxadiazole core acts as a π deficient moiety in D-A or D-A-D type flourophores with small Δ_{ST} for efficient emission [46] .

Hence two new1,3,4 oxadiazole derivatives BOPOXD and BPHOXD were synthesized according to scheme 1 and these molecules were taken for the doping onto chitosan matrix.



Scheme.1. Synthetic route for BOPOXD and BPHOXD

2.2 Method

The procedure followed here is solvent intercalation technique. Chitosan composites were prepared by dissolving 0.5 g of chitosan in 25 ml of 2% acetic acid, stirred in a magnetic stirrer for about one hour, the dopants BOPOXD (5-[4-(benzyloxy) phenyl]-1, 3, 4-oxadiazol-2-amine) and BPHOXD (2-([1, 1'-biphenyl]-4-yl)-5-[(4-bromophenyl) methyl]-1, 3, 4-oxadiazole)were weighed as 0.01 g, 0.02g, 0.03 g and made a slurry using ethanol, the slurry was added to the transparent polymeric solution of chitosan and ultrasonicated for 3 hr. The polymeric solution containing BOPOXD and BPHOXD was uniformly spread over petridish, annealed at a temperature of 50^{o}C for 24 hr. The films were cooled to room temperature, slowly peeled off from the petridish.

2.3 Results

The multifunctional chitosan films were fabricated by doping of 5-[4-(benzyloxy) phenyl]-1,3,4-oxadiazol-2-amine (BOPOXD) and 2-([1,1'-biphenyl]-4-yl)-5-[(4-bromophenyl) methyl]-1,3,4-oxadiazole (BPHOXD), by solvent intercalation method. The doping was confirmed by FTIR, SEM and EDS data. The dopant molecules are dispersed as micro and macrocrystals in the chitosan matrix. The dopant BOPOXD encapsulated into chitosan matrix by intermolecular H-bonding resulted in red shift (261nm to 340nm) of λmax. The crystallinity of the doped films increased in dose- dependent manner. The luminescent measurements of doped chitosan films were carried out at their own excitation wavelength of 340nm and 260nm for BOPOXD and BPHOXD doped films respectively. It resulted in emission spectra with λ_{max} ranging between around 446nm-455nm and 426nm-452nm in an increasing order of dopant concentration for BOPOXD and BPHOXD. The non-luminescent films turned out to be excellent photoluminescent materials on doping; with maximum intensity at 4wt% dopant concentration for both the dopants.

CHAPTER 3

The structural and photoluminescence studies of 2-[(4-tert-butylphenyl)-5–(4-biphenyl)]-1, 3, 4- oxadiazole (PBD) incorporated *γ* ray irradiated chitosan films

3.1 Introduction

Ionizing radiation, such as gamma rays, is used in a variety of fields, including nuclear science, medicine, metallurgy, the food industry, and the environment [47]. Gamma-ray radiation, on the other hand, is well established to be extremely harmful to human health. As a result, developing simple and easy-to-use systems for sensitive and rapid detection of gamma ray radiation is both desirable and necessary [48]The naturally occurring polymer undergoes crosslinking or chain scission under the ionizing process[49][50][51]. The formation of crosslinked material from natural polymers and their derivatives opens a window for applications of such materials in many areas. The main role of gamma irradiation is to create microstructural change in the film or the bulk material[52][53][54]. Such changes depend on the number of gamma quanta and internal structure of material. This in turn changes their physical properties and makes them attractive materials for a variety of applications such as optoelectronics, sensors, tissue engineering etc.

The conventional crosslinking method involves toxic additives to bring about polymerization process, hence losses its biocompatibility. Ionizing radiation has the unique ability to start

polymerization or crosslinking reactions without the use of toxic chemicals. As a result, radiation processing is proving to be an excellent tool for medical applications and optoelectronic applications.

Detection of ionizing radiation using plastic scintillators has been a field of interest. In this case, we take interest in the development of polymeric materials, called plastic scintillators, which allow the detection of ionisation radiation at low costs than inorganic-based scintillating devices. In a few words, a plastic scintillator is composed of a polymer matrix embedding one or several fluorescent molecules[55].

Oxadiazole derivatives were widely reported as ideal Electron Transport (ET) /Hole Blocking (HL) materials in organic optoelectronic devices. Oxadiazole was not only used as an ET unit in fabricating good ET materials for its high mobility of electrons, but also as a good HB unit in fabricating good HB materials resulting in a wide band gap [56]. It was observed that the oxadiazole molecule had altered the polymer property of the chitosan. So a study on the effect of irradiation on oxadiazole/chitosan composites was device with a known OLED material 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD).

So the present work carried out with the following objectives

- To prepare PBD doped chitosan films by solvent casting technique.
- To subject these films for gamma irradiation
- To study the physical properties of films after irradiation
- To carry out UV and photoluminescence studies

3.2 Method

The procedure followed here was the solvent intercalation technique. The chitosan (0.5g) was weighed. The weighed polymer was dissolved in the respective solvent and stirred 24hr to get homogeneity. The slurry of the dopant 2-(4-tert-butylphenyl)-5-4-biphenyl)-1, 3, 4-oxadiazole (PBD, 4%) was made using ethanol. This prepared slurry was slowly added to the clear polymer solutions and ultrasonicated for one hour. After sonication, the mixture was vigorously stirred at 950rpm for the uniform distribution of the dopant in the polymer solution. The reaction mixture was poured onto a Petri dish and annealed at a temperature of 60^0C. After drying, the films were removed and preserved in a desiccator for further analysis. These films were taken for gamma irradiation of different dosage (15kGy, 30kGy, 45kGy) and these films were designated as CHPBD.

3.3 Results

Herein, versatile biopolymer chitosan films doped with 2-[(4-tert-butylphenyl)-5–(4-biphenyl)]-1, 3, 4- oxadiazole (PBD) a known OLED material were prepared by intercalation method. The dopants uniformly intercalated in the polymer matrix which brought about changes in the morphology and mechanical properties. This was evidenced by SEM images. In PXRD, peaks centred on 2θ, 21.24^0 for pristine chitosan film, but for the unirradiated CHPBD, it was shifted to the lower angle 16.09^0 to form amorphous film. However, for the irradiated CHPBD shifting to the higher angle 22.9^0, 23.08^0, 27.23^0 suggesting that dopant had chemically interacted with the polymer matrix. The Young's modulus, tensile strength indicated supportive properties. An interesting change in UV absorption behaviour was observed for the unirradiated CHPBD exhibiting λ_{max} at 290nm with a hypsochromic shift with respected to dopant (λ_{max},309nm). This indicated weak head-to-head alignment of dyes in an unirradiated matrix; whereas irradiation brought about changes through chemical crosslinking in the architecture of films with a redshift to 309nm. Hyperchromism was also the effect of irradiation on films. The unirradiated films exhibited emission maxima around 369nm whereas irradiated films showed 412nm. Hence, a simple method was developed for the preparation of blue emissive biopolymeric materials.

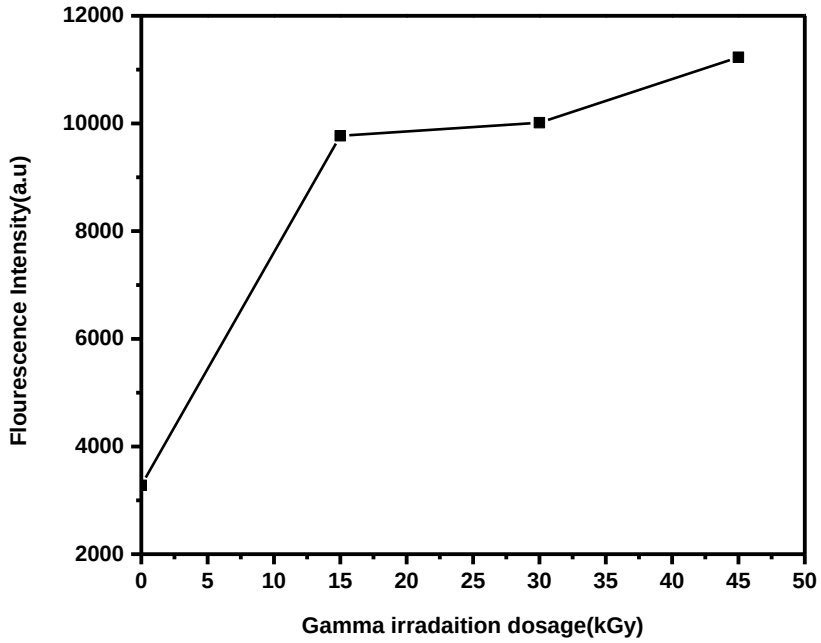


Fig.6. Variation of fluorescence intensity with irradiation dose (CHPBD films)

CHAPTER 4

The structural, UV and photoluminescence studies of 4,4'-bis(9*H*-carbazol-9-yl) biphenyl (CRB) incorporated *γ* ray irradiated chitosan films.

4.1 Introduction

Fluorescence detection is known for its sensitivity and simplicity of use [57]. As a result, fluorometry for gamma-ray radiation has recently got a lot of attention [58]. Studies on fluorescence turn off sensor for gamma irradiation using a combination of the aggregation-induced emission (AIE) behaviour of silole molecules and cleaving of in polymers containing $–SO_2$ groups in the main chain by gamma-ray irradiation was reported.

This work is also focused on fluorescence quenching for the gamma ray sensing. One of the hole transport materials i.e.,4,4'-bis(9*H*-carbazol-9-yl) biphenyl (CRB) is taken as a dopant for this polymer matrix. This organic molecule is commonly used in PhOLED (phosphorescent OLED) due to its high triplet energy (2.57eV) [59]. The effect of gamma irradiation on CRB as a dopant in the chitosan polymer matrix is undertaken for the studies.

4.2 Method

The solvent intercalation technique was used for fabrication of CHCRB films. The 0.5g of chitosan dissolved in the respective solvent. Stirred for 24 hr. to obtain homogeneity and the slurry of the dopant 4,4'-bis(9*H*-carbazol-9-yl) biphenyl (CRB) was made using ethanol. This prepared slurry was slowly added to the clear polymer solutions and ultrasonicated for one hour. After sonication, the mixture was vigorously stirred at 950 rpm for the uniform distribution of the dopant in the polymer solution. Then the mixture was poured into a Petri dish and annealed at a temperature of 60^0C. After drying, the films were removed and preserved in a desiccator for further analysis.

4.3 Results

In this work, 4,4'-bis(9*H*-carbazol-9-yl) biphenyl (CRB) incorporated *γ* ray irradiated chitosan films were prepared by solvent casting technique. These film shows changes in the properties due to different dosage of gamma irradiation. Structural confirmation was done by FTIR, SEM. Thermal stability was conducted by Thermo Gravimetric Analysis. Crystallinity study was done by PXRD. The UV and Photoluminescence studies were carried out for the irradiated and unirradiated films. The λ_{max} for the fabricated non irradiated was 301nm and

also for irradiated it gave same value. The dopant intercalates physically with in the matrix as there were no active bonds in the molecule to form radical upon gamma irradiation. It was reflected by no shift of λ_{max} (301nm) for the unirradiated and irradiated films. But the absorption intensity increased in the films. The XPS also showed only peak corresponding to NH_2 was observed at 400eV indicating that no chemical changes occurred during intercalation.

The photoluminescence graphs showed interesting phenomenon of quenching in emission intensity upon irradiation with λ_{max} 392nm (UVA region). Unlike in the case of oxadiazole doped films where emission intensity increased with bathochromic shift, here no such changes were observed. The fluorescence quenching could be attributed to the transfer $H^{\cdot}$ from chitosan matrix to CRB to form radical ion which further recombine to form radical ion polaron pairs.

These results lead to two inferences

i) The UV emitting chitosan films could be fabricated by doping carbazole derivative into chitosan matrix which could be used in optoelectronic devices and UV LED layers.

ii) The same film could be used as on-off sensor for detecting highly ionizing gamma radiation (fig.7).

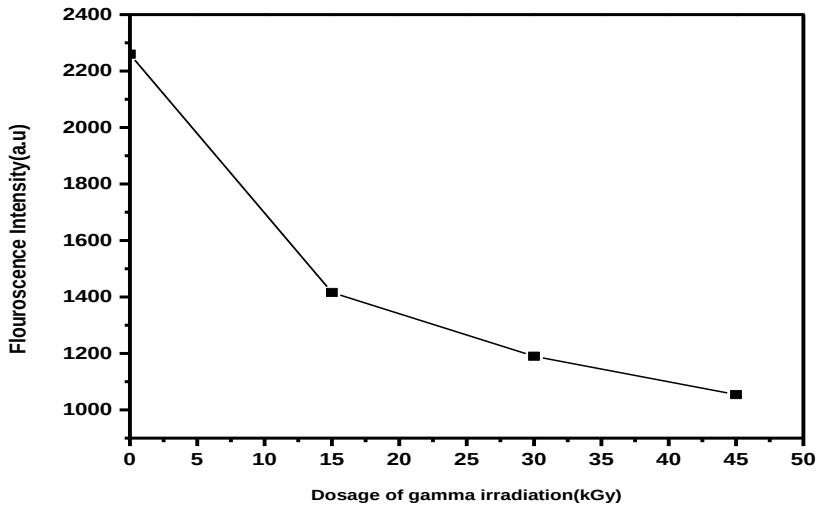


Fig.7. Variation of fluorescence intensity with irradiation dose (CHCRB films)

CHAPTER 5

Design, fabrication and studies on optical properties of new hybrid chitosan films doped with 3-hydroxyflavone (3HF).

5.1 Introduction

Construction of WOLEDs generally requires the use of two (blue and yellow) or three (blue, green, and red) different colour emitters, covering the whole visible light range from 400 to 700 nm to achieve good colour rendering. This requirement often leads to complex device architectures, demanding fabrication processes and high cost in order to accommodate multiple emissive materials. In contrast to systems composed of several fluorescent molecules, single-molecular systems with white emission through double emission DE have several advantages: they can avoid the drawbacks of phase separation, colour aging, and degradation; moreover, they lead to enhanced reproducibility and stability, as well as simpler device fabrication. This dual emission phenomenon initially existed in azulene [60]. Lippert et al. investigated the DE phenomenon in intramolecular charge transfer (ICT) states in a push–pull 4-N,N-dimethylaminobenzonitrile (DMABN) compound in 1959[61]. Singlet DE can also result from the presence of dual CT states, excimer states, excited state intramolecular proton transfer (ESIPT), and structural changes in the emitter caused by UV light absorption.

So, in this work, 3HF was taken as a dopant to enhance fluorescence activity of biopolymer chitosan. Biopolymer chitosan films doped with 3HF (2%, 4%, 6%) were fabricated by solvent intercalation technique. The fabricated composite films were characterized which confirmed the successful doping. Upon determining the photoluminescence property of these films; exhibited dual emission with large stokes shift and increased quantum yield. So these blue (Emax, 472nm) and green (Emax 530nm) emissive films could find use in devising environment friendly WOLED. this work focused on the application of biopolymer in WOLED. So dual emitter is taken as a dopant for the chitosan matrix.

5.2 Method

The procedure followed here is solvent intercalation technique. Chitosan composites were prepared by dissolving 0.5 g of chitosan in 25 ml of 2% acetic acid, stirred in a magnetic stirrer for about one hour, the dopants 3-hydroxy flavone were weighed as 0.01 g, 0.02g, 0.03 g and made a slurry using ethanol, the slurry was added to the transparent polymeric solution of chitosan and ultrasonicated for 3 hr. The polymeric solution containing 3-hydoxy flavone was uniformly spread over Petri dish, annealed at a temperature of 50^{o}C for 24 hr. The films were cooled to room temperature, slowly peeled off from the Petri dish.

5.3 Results

Biopolymer chitosan composite films doped with dual emitter (DE) 3-hydoxyflavone were prepared by solvent intercalation method. The FTIR, SEM, PXRD and TGA techniques were used to characterize the films. The surface morphology, crystallinity and stability of the films improved as the dopant concentration increased. The UV absorbance maxima of the films found at 329nm and 418nm as dual absorption with a bathochromic shift with respect to dopant absorption maxima 305nm and 340nm. This was attributed to binding of 3-hydroxy flavone to the polymer matrix. Similarly, emission maxima were found at 472nm and 530nm, on shining them at 329nm. As a result, non-luminescent chitosan films changed to be effective photoluminescent material of dual emission with large stokes shift of 143 nm for band I and 112nm for band II. The relative quantum yield of doped composite films were found to be in the range of 30.15% to 37.05%. Hence, these films with blue and green emission would find use as white light emitting diode materials.

CHAPTER 6

Effect of Nano ZnO Doping on Structural, Morphological and Luminescent Properties of Pullulan Films

6.1 Introduction

In recent years polymer nanocomposites have been attracted in the field of science and technology, as it shows ability to harness unique material properties. It is well known that polymeric materials with high dispersion capacity serve as host matrices for the inorganic materials. However, biopolymer possesses natural electrical and optical properties which

could be enhanced by crosslinking with suitable chromophore and also it is conventional for the man made polymers [62].

Pullulan is a water-soluble exopolysaccharide produced from bacterial fungi and it is biodegradable, nontoxic. Due its high transparency nature, it can be used as a host matices for the inorganic and organic materials. In recent years, the nanostructured ZnO NPs with their large surface area have tremendous application in the field of optoelectronics, sensors, photocatalysis. However, polymeric matrix incorporated with high photostable metal oxides is more vital. In the present investigation, the biosynthesized ZnO Nps was incorporated into the biopolymer pullulan and studied its luminescence nature.

6.2 Method

All chemicals were of analytical grade and used without further purification. In the typical procedure, the aqueous fruit extract of *Syzygium samarangense* was prepared by boiling finely chopped fruits (10 g) with 100 ml of deionized water, at 80˚ C for about 30 minutes. Then the extract was filtered using Whatmann filter paper. ZnO NPs were synthesized by hydrothermal method using aqueous solution mixture of 0.1 M Zinc Acetate and 20 ml of fruit extract kept at 80º C for 5 hrs. After the reaction, the product was thoroughly washed and dried in hot air oven at 60° C overnight.

Synthesized ZnO Nps was doped into the polymer solution in different weight percentage (2wt%,4wt%,6wt%) and this polymer solution was ultrasonicated for about two hours. The complete ZnO NPs dispersed polymer solution was slowly poured into petridish. The petridish was annealed at 60^0C for the complete drying of the film. After drying, films were slowly removed from the petridish.

6.3 Results

Herein, the pristine and nano ZnO doped pullulan films are fabricated by solution intercalation technique. The ZnO Nps were synthesized by hydrothermal method using *Syzygium samarangense* fruit extract as a surfactant. The effect of nano ZnO doping on structural, morphological and luminescent properties of fabricated films was studied. The XRD study reveals the increase in the crystallinity of the films after the dispersion of nano ZnO in the film. While the structural aspects are probed by FTIR analysis. The FESEM image shows the morphological changes due to the addition of nano ZnO into the polymer matrix. The presence of nano ZnO in the film is confirmed by EDX analysis. The pristine

film was transparent in UV region. Incorporation of ZnO Nps into the polymer matrix enhances its absorbance nature by showing shoulder shaped peak at 355nm. Appearance of new peak on doping attributed to the formation of charge transfer complex between ZnO Nps and polymer matrix. The optical study including UV analysis and Photoluminescence (PL) revealed the dependence of luminescence nature of pullulan films on nano ZnO doping. The films were excited at 355nm. The pure pullulan film showed non emissive curve. Fabricated doped films showed two emissive peaks at 413nm and 439nm corresponds to near band edge (NBE) emission, originating from the recombination of the free excitons of ZnO Nps. These studies revealed the dependence of luminescence nature of pullulan films on nano ZnO doping.

CONCLUSION

In summary, Total 30 films were prepared and characterized by SEM, PXRD, FTIR and TGA. The preparation of polymer composites was carried out by solvent casting method. Two new 1,3,4 -oxadiazole derivatives were synthesized and doped into chitosan matrix to cast composite films. These films exhibited emission in blue region. In another set of experiments, the gamma irradiation technique was used to crosslink commercially available oxadiazole [PBD] and carbazole [CRB] derivatives which were doped into the chitosan matrix. The irradiation of the doped films with gamma rays changed morphology as well as optical properties by radical mediated reactions. The PBD doped films exhibited enhancement of photoluminescence intensity whereas CRB doped films exhibited quenching of PL. This behaviour could be related to arrangements of the dopants in the matrix either chemical or physical intercalation under the influence of irradiation. The doping of dual emitter 3HF to chitosan matrix resulted in dual emitting films with large Stokes shift. Another set of blue emissive films were fabricated by doping of ZnO nanoparticle to Pullulan. In addition to it, the designed composites unveil the increase in the value of refractive index, extinction coefficient, optical conductivity, dielectric constant. These results, therefore, evidenced in new approach for the fabrication of chitosan and pullulan composites for the specific application in optical devices with desired optical properties. The non-luminescent films turned out to be excellent blue light emitting photoluminescent materials on doping. This widened the scope of its utility as a versatile functional material.

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List of Publications

1. **Pushparekha**, Balladka Kunhana Sarojini, Kabiru Bello, Bantwal Shivarama Holla, Murari Mudiyaru Subrahmanya. (2019) Design, fabrication and studies on optical properties of new hybrid chitosan films doped with 1, 3, 4-oxadiazole derivatives for down conversion and photoluminescence applications. ***Optical Materials*** 89, 80–91. https://doi.org/10.1016/j.optmat.2018.12.054
2. **Pushparekha**, Balladka Kunhanna Sarojini, Shreedatta Hegde (2021) The structural studies of 2-[(4-tert-butylphenyl)-5–(4-biphenyl)]-1, 3, 4- oxadiazole (PBD) incorporated γray irradiated chitosan films for optoelectronic applications ***Journal of Molecular Structure*** 1242 (2021) 130699. https://doi.org/10.1016/j.molstruc.2021.130699
3. **Pushparekha**, Balladka Kunhanna Sarojini, and U. Vinoditha (2020) Effect of nano ZnO doping on structural, morphological and luminescent properties of pullulan films ***AIP Conference Proceedings*** 2244, 020004; https://doi.org/10.1063/5.0009077
4. Niveditha, N.B**.,** Sarojini, B.K., **Pushparekha** and Bello, K. (2020). Customized eco-friendly UV-B filtering films from vital collagen isolated from Arabian Sea fish Indian oil sardine (*Sardinella longiceps*). ***AIP Conference proceedings***. *2244*, 020003; https://doi.org/10.1063/5.0009427.
5. Sarojini, B.K. Niveditha, N.B**.** and **Pushparekha**. (2020). **Book chapter** on Emerging trends in the synthesis, properties and applications of Nanogels derived from Pullulan, Collagen and Gelatin. Gels Horizons: From Science to Smart Materials (In Press).

Paper presented in National/ International Conferences

1. **Pushparekha** and B. K. Sarojini, Preparation and characterization of tailor made chitosan hydrogels and films for the drug delivery of oxadiazole amine derivatives presented in the International conference on Green chemistry and nanotechnology opportunities and challenges 2017. St Aloysius College Mangaluru.
2. **Pushparekha**, B.K.Sarojini and Anupam. G. An Experimental and Theoretical Study on 1, 3, 4-oxadiazole doped chitosan films, Reaching the unreached through science and technology: Recent Advances in Physical, Chemical, mathematical and Biological Science for Energy, Health and Environment, Mangalore University, Mangalagangothri, held from 8-9th September 2017.
3. **Pushparekha**, B. K. Sarojini and M. Krishna Kishore. Investigation on I-V characteristics of newly synthesized 6-[(*E*)-(6-nitro-1, 3-benzothiazol-2-yl)diazenyl]naphthalen-1-ol(NBDN) doped pullulan for OLED applications, presented in the National conference on Advanced Materials for Health, Energy and Environment TEQIP-III, JSS science and technology University, Mysore, 2018.
4. **Pushparekha** and B.K. Sarojini. The study of opto-electrical property of 2-(4-tert-butylphenyl)-5-4-biphenyl)-1, 3, 4-oxadiazole (PBD) doped pullulan films for optoelctronic applications presented in 37th Annual conference Indian Council of chemist at Department of Chemistry at NITK, Surathkal, 2018.
5. **Pushparekha**, Balladka Kunhanna Sarojini, and U. Vinoditha. Effect of nano ZnO doping on structural, morphological and luminescent properties of pullulan films. International Conference on Physics of Materials and Nanotechnology (ICPN 2019). Department of Physics, Mangalore University.

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